

cy 4



INVESTIGATION OF THE EFFECTS OF FLUORINE ON CRYOPANEL MATERIALS FOR SPACE CHAMBER PROPULSION TESTS

P. G. Waldrep and D. M. Trayer

ARO, Inc.

September 1968

This document has been approved for public release
and sale; its distribution is unlimited.

**AEROSPACE ENVIRONMENTAL FACILITY
ARNOLD ENGINEERING DEVELOPMENT CENTER
AIR FORCE SYSTEMS COMMAND
ARNOLD AIR FORCE STATION, TENNESSEE**

PROPERTY OF U. S. AIR FORCE
AEDC LIBRARY
F40600-62-C-0001

44

NOTICES

When U. S. Government drawings specifications, or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise, or in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Qualified users may obtain copies of this report from the Defense Documentation Center.

References to named commercial products in this report are not to be considered in any sense as an endorsement of the product by the United States Air Force or the Government.

INVESTIGATION OF THE EFFECTS OF FLUORINE
ON CRYOPANEL MATERIALS
FOR SPACE CHAMBER PROPULSION TESTS

P. G. Waldrep and D. M. Trayer
ARO, Inc.

This document has been approved for public release
and sale; its distribution is unlimited.

FOREWORD

The research presented in this report was sponsored by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 62302F, Project 5730, Task 573004.

The results were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator for AEDC under Contract F40600-69-C-0001. The research was conducted from January to August 1967 under ARO Project No. SW5705. The manuscript was submitted for publication on July 15, 1968.

The authors gratefully acknowledge the assistance of the Metallurgy Department of the Oak Ridge Gaseous Diffusion Plant, which is operated for the U. S. Atomic Energy Commission by Union Carbide Corporation, Nuclear Division, Oak Ridge, Tennessee. This laboratory performed the analyses of the test specimens. The authors also acknowledge the valuable assistance of S. G. Walker, W. H. Owens, and J. R. McCabe of the Chemical and Metallurgical Branch and of H. L. Henderson of the Central Engineering Branch of the Engineering Support Facility, ARO, Inc.

This technical report has been reviewed and is approved.

Eules L. Hively
Research Division
Directorate of Plans
and Technology

Edward R. Feicht
Colonel, USAF
Director of Plans
and Technology

ABSTRACT

The extent of corrosion by fluorine (F_2) on several cryopanel materials was evaluated for conditions approximating those which might be expected in a space simulation chamber during rocket engine tests. Four torr of F_2 pressure was applied at room temperature, and specimen temperatures were cycled between ambient and $77^\circ K$. The chamber was periodically pumped to high vacuums. The total exposure time exceeded 1000 hr. Type 304L stainless steel, phosphorus deoxidized copper, and 1100 aluminum were tested. Some specimens were welded, and some were tested with an applied bending stress. No pitting or other microstructural corrosion was detected, but noticeable changes occurred in the surface appearance, especially with aluminum and copper.

CONTENTS

	<u>Page</u>
ABSTRACT.	iii
I. INTRODUCTION	1
II. TEST EQUIPMENT	
2.1 Chamber	2
2.2 Pumping System	3
2.3 Specimen Holder	3
2.4 Fluorine Addition System	4
2.5 Fluorine Pumpout System	4
III. TEST SPECIMENS	
3.1 Welding Methods	5
3.2 Stressing Method	5
3.3 Stainless Steel 304L Shim Specimens	5
3.4 Copper Specimens, Brazed and Unbrazed	6
3.5 Copper and Stainless Steel Composite Specimens	6
3.6 Aluminum Shim Specimens.	6
3.7 Stainless Steel Cryopanel Specimen.	7
IV. OPERATIONAL PROCEDURES	
4.1 Cleaning and Passivation of Chamber and Internal Components	7
4.2 Operation during Corrosion Test	7
V. EVALUATION OF TEST SPECIMENS	
5.1 Electron Probe Microanalysis	9
5.2 X-Ray Diffraction.	9
5.3 Total Fluoride Analysis	9
5.4 Metallographic Examination	9
VI. RESULTS AND DISCUSSION	
6.1 Stainless Steel 304L Shim	10
6.2 Copper Specimens	12
6.3 Copper/Stainless Steel Composite Specimens	13
6.4 Series 1100 Aluminum Specimens	14
6.5 Stainless Steel Cryopanel Specimen.	14
VII. SUMMARY AND CONCLUSIONS	15
REFERENCES	16

TABLES

I. Total Fluoride Analysis of Test Specimens	10
II. Fluoride Concentration by Microprobe Analysis	11

APPENDIX **Illustrations**

<u>Figure</u>	<u>Page</u>
1. Fluorine Corrosion Test Chamber Schematic.	19
2. 2- by 1.5-Foot Research Vacuum Chamber	20
3. Specimen Holder	21
4. Specimens Mounted on Holder	21
5. Schematic Views of Specimens Stressed for F ₂ Corrosion Testing	22
6. Unwelded Stainless Steel 304L Specimen, Exposed to F ₂ , 2X	23
7. Welded Stainless Steel 304L Specimen, Exposed to F ₂ , 2X	23
8. Control, Unwelded Stainless Steel 304L, Unexposed, 500X.	24
9. Unwelded Stainless Steel 304L, Exposed to F ₂ , 500X.	24
10. Control, Welded Stainless Steel 304L, at Weld, Unexposed, 500X	25
11. Welded Stainless Steel 304L, Stressed, at Weld, Exposed to F ₂ , 500X	25
12. Welded Stainless Steel 304L, Stressed, Away from Weld, Exposed to F ₂ , 500X	26
13. Unwelded Copper Specimen, Exposed to F ₂ , 2X	26
14. Braze Copper Specimen, Exposed to F ₂ , 2X	27
15. Control Copper Specimen, Away from Braze Joint, Unexposed, 500X	27
16. Unwelded Copper Exposed to F ₂ , 500X	28
17. Braze Welded Copper, Near Weld, Stressed, Exposed to F ₂ , 500X	28
18. Toe of Phosphor Bronze Weld, Stressed, Exposed to F ₂ , 500X	29
19. Center of Phosphor Bronze Weld, Stressed, Exposed to F ₂ , 500X	29

<u>Figure</u>	<u>Page</u>
20. Copper-Stainless Composite Specimen, Exposed to F ₂ , 2X	30
21. Control Specimen, Copper Side of Nickel Weldment, Unexposed to F ₂ , 500X	30
22. Control Specimen, Stainless Steel Side of Nickel Weldment, Unexposed to F ₂ , 500X	31
23. Copper Side of Nickel Weldment, Exposed to F ₂ , Stressed, 500X	31
24. Stainless Side of Nickel Weld, Exposed to F ₂ , Stressed, 500X	32
25. Copper Shim Portion of Composite Specimen, Away from Weld, Exposed to F ₂ , Stressed, 500X . .	32
26. Stainless Shim Portion of Composite Specimen, Away from Weld, Exposed to F ₂ , Stressed, 500X . .	33
27. Aluminum Specimen, Exposed to F ₂ , 2X.	33
28. Control Specimen, Unexposed Aluminum, 500X. . . .	34
29. Aluminum Exposed to F ₂ , 500X.	34
30. Control, Stainless Steel Cryopanel, Unexposed, 500X .	35
31. Stainless Steel Cryopanel, Exposed to F ₂ , 500X . . .	35

SECTION I INTRODUCTION

During rocket engine tests in space simulation chambers, the installed cryopanel will be subjected to intimate contact with a variety of corrosive chemicals from the propellants and reaction products. In particular, the hypergolic propellants and many of the associated reaction products are highly corrosive and could lead to eventual failure of the cryopanel materials.

The most reactive of the elemental oxidizers is fluorine (F_2). Fluorine reacts with all metals and most other elements, including some of the noble gases. Rocket engines using F_2 or fluorine compounds as oxidizers have operated at very high specific impulses and show real promise for future space applications. Because of the high reactivity of these oxidizers, however, there has been some reluctance to utilize them fully. Fortunately, however, with many metals the surface reactions form an impermeable, passive fluoride film, making it possible to handle F_2 and the fluorine class of compounds in propulsion systems as long as passivity is maintained. It seems probable that this class of oxidizers will find increasing application as technology advances and as experience is gained in their use.

To date, much has been done in understanding the behavior of materials when exposed to F_2 . Numerous studies have been made on the compatibility of various metals with fluorine propellants (Refs. 1 through 8). Several compilations have been published reporting the results of studies of this nature (Refs. 9, 10, and 11). Usually, these investigations are concerned with the behavior of materials to liquid fluorine (LF_2) at cryogenic temperatures or to gaseous fluorine (GF_2) at high pressures. They often apply to storage vessels or to transfer systems which are in contact with F_2 at rather high flow rates. The conditions studied have rarely approached those found in a space simulation chamber during rocket firing sequences. Thus, for widely differing exposure conditions, an extrapolation of previously existing data is uncertain and could lead to erroneous conclusions. For instance, the effects of high vacuum and cryogenic temperatures on passive fluoride films are unknown. Cracking or flaking of passive films may occur because of the differences in thermal expansion between the films and the substrate metal. There are some indications that corrosion films become thinner in a vacuum (Ref. 12). These actions could lead to continued attack by corrosive gases on the underlying metal surfaces. The integrity of the passive fluoride film is of fundamental importance in the resistance of

metal surfaces to progressive attack by F_2 , since any failure of the film could lead to rapid and destructive reaction at the site of the failure.

The intent of this test was to assess the effects on commonly used cryopanel metals exposed to an F_2 environment in combination with periodic application of vacuum and temperature cycling between 77°K and ambient.

The following exposure conditions were employed:

1. Fluorine gas pressures at room temperature of 4.0 to 4.2 torr. Total exposure time under this condition was approximately 957 hr.
2. Test specimens at liquid-nitrogen (LN_2) temperatures ($<85^\circ K$). Chamber pressure dropped by cooling and condensation to around 3.3 torr. Total exposure time under this condition was approximately 101 hr.
3. Test specimens warming or cooling between ambient and LN_2 temperatures. Pressures varying between 3.3 and 4 torr. Exposure time approximately 18 hr.
4. The specimens were taken through 11 complete temperature cycles in the presence of F_2 .

Three basic types of specimens were tested: stainless steel type 304L, phosphorus deoxidized copper, and type 1100 aluminum.

SECTION II TEST EQUIPMENT

2.1 CHAMBER

The 2- by 1.5-Foot Research vacuum chamber was used for this test. The chamber (Figs. 1 and 2, Appendix) is a stainless steel bell jar with a free volume of 139 liters. The specimen holder was inserted through an opening in the top. Fluorocarbon O-rings lubricated with fluorocarbon grease were used for vacuum sealing the chamber ports and flanges.

2.2 PUMPING SYSTEM

The chamber is equipped with a mechanical pump, an ion getter pump, and LN₂-cooled cryopumps. The mechanical pump is equipped with a stainless steel, cylindrical F₂ trap 3 ft long and 4 in. in diameter and filled with granular soda lime. An LN₂-cooled oil vapor trap is provided between the mechanical pump and the F₂ trap. The ion-getter pump has a pumping speed of about 400 liters/sec in the 10⁻⁶-torr pressure region and can pump the chamber to 10⁻⁷ torr. A cylindrical shroud surrounding the specimen holder and the specimen holder itself were cooled with LN₂ and acted as cryopumps.

Chamber pressures were measured in the vacuum region with a thermocouple gage and an ion gage. Fluorine gas pressure in the chamber was measured with a variable reluctance pressure transducer with a strip chart readout. The transducer was operated from 0 to 5 torr. The mechanical pump was used for a reference and null-point vacuums on the pressure transducer.

2.3 SPECIMEN HOLDER

The specimen holder (Fig. 3) was a stainless steel cylinder 10 in. long and 1.25 in. in diameter to which four longitudinal metal fins were welded. The fins, two of copper and two of stainless steel, served as mounts for the test specimens. One end of each specimen was sandwiched between a holder fin and a metal strip cut and drilled to match the fin. Specimens were bolted between the fins and strips. Copper screws and bolts were used for attachments to copper fins and stainless steel screws and bolts for the stainless steel fins. Specimens are shown mounted to the holder in Fig. 4.

Liquid nitrogen circulated through the cylindrical portion of the specimen holder during cooling. Fin temperatures were measured with stainless steel sheathed thermocouples attached near the ends of the fins.

When inserted in the chamber, the holder was surrounded by a cylindrical stainless steel LN₂-cooled shroud. The shroud was open at the ends for access of corrosive vapor.

2.4 FLUORINE ADDITION SYSTEM

Fluorine gas* was supplied from a commercial gas cylinder equipped with a single stage regulator for F_2 service. The gas was transferred through 0.25-in. copper lines having flared connections. The line valves were the bellows seal type with fluorocarbon gaskets and stem points. Hydrogen fluoride (HF) was removed from F_2 by passing the gas through a dry sodium fluoride trap.

Fluorine line pressures were measured with a Bourdon® gage. Chamber pressures were monitored during F_2 addition with the pressure transducer.

2.5 FLUORINE PUMPOUT SYSTEM

Fluorine gas was pumped from the chamber through a cylindrical stainless steel trap filled with granular soda lime. The 4-in. -diam by 3-ft-long trap was equipped with bellows seal valves having fluorocarbon seats and gaskets.

SECTION III TEST SPECIMENS

All test specimens, except the stainless steel cryopanel section, were cut from 0.020-in. -thick commercial shimstock. The specimens were 1 in. wide and 2 in. long. Half of each specimen was inserted between the holder fin and clamping strip, leaving 2 in.² of surface available for direct corrosion exposure. Mounted specimens are shown in Fig. 4.

The types of specimens tested were as follows:

1. Type 304L stainless steel, with and without weldments and with and without applied bending stress.
2. Phosphorus deoxidizer copper, brazed and not brazed, with and without applied stress.
3. Composite specimens of copper welded to type 304L stainless steel with nickel welding wire, stressed and unstressed.

*Matheson-compressed F_2 gas of 98-percent purity was used.

4. 1100 aluminum, unstressed.
5. Stainless steel (304L) cryopanel section, unstressed.

A total of 43 specimens were tested. Thirty-four of these were welded or brazed by the techniques described in Section 3.1. Twenty-two specimens, all welded or brazed, were tested with an imposed bending stress as described in Section 3.2.

3.1 WELDING METHODS

Specimens to be welded were machine cut along a line parallel to the specimen holder. The two pieces were then fitted into a special jig and clamped so that the cut edges corresponded. Argon gas was fed through the jig and onto the underside of the specimens at the weld point to minimize oxidation. Argon shielded welds were then made along the cut edges with a DC welder, hand feeding 0.035-in. - diam welding wire.

The stainless steel 304L specimens were welded with stainless steel type 308 ELC welding wire. Copper specimens were joined with phosphor bronze C wire (95-percent bronze and 5-percent tin). Copper was joined to stainless steel 304L with nickel wire.

3.2 STRESSING METHOD

External stressing was achieved by deflecting the tips of the specimens by a predetermined amount calculated to give a bending stress in the base metal of about 75 percent of the yield strength. The method is shown schematically in Fig. 5. Specimens were stressed in matched pairs of the same material. The two specimens were bolted into the holder fin at the same point but separated by a metal fin 0.060 in. thick. Thus, the surfaces were initially parallel. The tips were then deflected further apart by inserting a Teflon® wedge of measured thickness.

3.3 STAINLESS STEEL 304L SHIM SPECIMENS

Four pairs of welded stainless steel specimens were exposed in the stressed condition. Three welded stainless steel specimens were tested without external stressing, and three unwelded and unstressed stainless steel specimens were tested. All stainless steel specimens were attached to stainless steel 304L holder fins.

These specimens were cleaned before testing by wire brushing the weld beads followed by washing in reagent grade acetone and methanol and finally by ultrasonic cleaning and vapor degreasing in Freon MF®.

3.4 COPPER SPECIMENS, BRAZED AND UNBRAZED

Two pairs of externally stressed, brazed phosphorus deoxidized copper specimens were tested. Three unstressed, brazed specimens and three unstressed and unbrazed specimens were tested. All of these contacted copper fins during exposure.

The copper surfaces were cleaned by immersion at 80°C in an aqueous solution of 15-percent acetic acid and 0.2-percent Rodamine® inhibitor. Following this, the specimens were rinsed thoroughly in distilled water followed by acetone rinses. They were finally cleaned ultrasonically and vapor degreased in Freon MF.

3.5 COPPER AND STAINLESS STEEL COMPOSITE SPECIMENS

These specimens were prepared by joining phosphorus deoxidized copper shim to stainless steel 304L with nickel welding wire. The tips of these specimens were copper, and the bases, which attached to the holder fin, were stainless steel. They were welded along a line midway between the holder fin and the tip so that 1 in.² of each material was exposed.

Three stressed pairs were tested contacting a stainless steel fin and two stressed pairs contacting copper fins. In addition, three each of the unstressed specimens were tested contacting stainless steel and copper fins.

The stainless steel and weld portions were wire brushed to remove loose oxide. The copper portion was cleaned with inhibited aqueous acetic acid as described in Section 4.4. Following the acid cleaning and a thorough distilled water rinse, the specimens were immersed in multiple portions of reagent grade acetone and finished by ultrasonic cleaning and vapor degreasing with Freon MF.

3.6 ALUMINUM SHIM SPECIMENS

Three series 1100 aluminum shim specimens were exposed to the corrodent. All three contacted copper fins. No weldments were made on these, and they were unstressed. They were cleaned with multiple

rinses of acetone and methanol followed by ultrasonic cleaning and vapor degreasing in Freon MF.

3.7 STAINLESS STEEL CRYOPANEL SPECIMEN

A section of stainless steel 304L commercially fabricated cryopanel was included in the test. After removal from the cryopanel, the section, measuring 2 by 6-2/3 in., was fusion welded to seal all edges and 3/8-in. stainless steel lines welded into each end. These lines were then welded into the central cylinder of the specimen holder, thereby allowing LN₂ to flow from the cylinder through the specimen during cooling cycles. A sheathed thermocouple was attached to the surface. This specimen is shown in Fig. 4. It was cleaned after attachment to the holder by wire brushing the weld areas and rinsing with acetone and methanol. Final cleaning was done by ultrasonically cleaning and vapor degreasing the entire specimen holder in Freon MF.

SECTION IV OPERATIONAL PROCEDURES

4.1 CLEANING AND PASSIVATION OF CHAMBER AND INTERNAL COMPONENTS

The chamber, shroud, and F₂ traps were vapor degreased and acid cleaned before assembly. Fluorine lines were degreased with Freon MF. All small parts which would contact F₂, such as valves, feedthroughs, transducer ports, O-rings, and fittings, were degreased and cleaned with Freon MF in an ultrasonic cleaner. After cleaning, all assembly was done with clean room gloves to avoid excessive contamination.

After all components were assembled, the system was passivated with F₂ gas. One-half atmosphere of F₂ was admitted to the evacuated chamber and left for 24 hr. During this period infrared heat lamps were used to heat the chamber walls. At the end of this period the chamber was pumped to 10⁻⁶ torr and a fresh charge of F₂ admitted to a pressure of 0.5 atm.. This was left in the chamber overnight with the application of heat lamps. No drop in F₂ pressure during passivation was detected with the Bourdon pressure gage.

4.2 OPERATION DURING CORROSION TEST

After the specimens were placed in the chamber, the pressure was reduced to the 10⁻⁷-torr range with the ion-getter pump. Fluorine was

then bled into the chamber to a pressure of 4.1 torr as indicated by the pressure transducer readout. Specimen temperatures were periodically recorded.

At the beginning of a temperature cycle, the shroud was filled with LN_2 . The chamber pressure typically dropped about 0.5 torr after cooling the shroud. The pressure stabilized after about 5 min. The specimen temperature dropped to around 250°K in about 0.5 hr.

After the chamber pressure stabilized, the specimen holder was cooled with LN_2 . The temperature of the fins as indicated by thermocouples was about 85°K when the holder was fully cooled. After about 3-hr exposure at this temperature, LN_2 was purged from the holder and shroud with dry N_2 gas. In all instances, the holder was purged free of LN_2 before the shroud was emptied.

Every four or five days the gas was pumped from the chamber and a fresh charge of F_2 added to avoid accumulation of excessive amounts of HF.

SECTION V EVALUATION OF TEST SPECIMENS

The examination and analyses performed on the test specimens were done by the Metallurgy Department of the Oak Ridge Gaseous Diffusion Plant in Oak Ridge, Tennessee.

Evaluation consisted of the following steps:

1. A preliminary examination of all specimen surfaces under low magnification (10X to 20X) for evidences of corrosive attack,
2. Analysis of the corrosion films on selected specimens by electron probe microanalysis, X-ray diffraction, and by a colorimetric total fluoride method, and
3. Metallographic examination at magnifications of up to 1000X of sectioned and polished specimens for pitting, intergranular corrosion, and stress-corrosion cracking.

5.1 ELECTRON PROBE MICROANALYSIS

The corrosion films of several specimens were scanned for fluoride, using a Phillips Electron Probe Microanalyzer. Although this technique will not classify the exact chemical structures present in the films, some idea of the relative attack rate of F_2 on the different metals may be obtained. This technique also permitted comparisons of the relative degree of corrosion between localized areas of the specimens, e.g., base metal compared to weldments.

5.2 X-RAY DIFFRACTION

The surfaces of several specimens were scraped to remove the corrosion film and the scrapings examined by X-ray diffraction in an attempt to identify the chemical species present. This failed to yield identifiable patterns, probably because the films were too thin or the crystallite sizes too small to produce sharp diffraction lines.

5.3 TOTAL FLUORIDE ANALYSIS

The corrosion films from several specimens were treated by pyrohydrolysis and the resulting fluoride determined colorimetrically. This method yielded data on the total weight of fluoride present in the film. If identification of the corrosion products had been possible by the X-ray diffraction technique, this information could have been utilized to calculate a corrosion penetration depth. However, the lack of conclusive X-ray data makes this information of secondary importance.

5.4 METALLOGRAPHIC EXAMINATION

By far, the most accepted method of evaluating corrosion effects is by direct microscopic examination of specimen cross sections. The specimens were prepared for metallographic examination by mounting sections in a hard plastic resin, polishing, lapping, and, where necessary, etching.

The specimens were examined and photographed on a research metallograph. Unexposed control specimens were examined concurrently for comparison with the test specimens.

SECTION VI RESULTS AND DISCUSSION

6.1 STAINLESS STEEL 304L SHIM

Several of these specimens showed a light, hazy surface film. This is visible in Figs. 6 and 7. The film could not be identified by X-ray diffraction, but the presence of fluoride is verified by the total fluoride and electron microprobe analyses (Tables I and II). More fluoride was found on the welded specimens than on the unwelded (82 versus $65 \mu g F$). This is believed to be caused by a reaction between the oxides formed near the weld and F_2 rather than to an enhancement of the base metal reaction as a result of welding, since oxide was visibly present near the welds before exposure and could not be removed by vigorous wire brushing. The microprobe analysis demonstrated a higher concentration of fluoride in the weld region than in the metal away from the weld.

TABLE I
TOTAL FLUORIDE ANALYSIS OF TEST SPECIMENS

<u>Materials</u>	<u>Total Fluoride, μg</u>
Stainless Steel, 2 in. ²	65
Stainless Steel, Welded, 2 in. ²	82
Stainless Steel, Welded, 2 in. ²	92
Copper, 2 in. ²	98
Copper, Brazed, 2 in. ²	132
Copper, Brazed, 2 in. ²	136
Composite, Copper Side, 1 in. ²	35
↓	32
↓	29
↓	52
Composite, Stainless Side Including Nickel Weld, 1 in. ²	36
↓	49
↓	46
↓	44
Aluminum	460
Aluminum, 2 in. ²	460
Copper, 2 in. ²	98
Copper, Brazed, 2 in. ²	132
Copper, Brazed, 2 in. ²	136

TABLE I (Concluded)

<u>Materials</u>	<u>Total Fluoride, μg</u>
Copper Side of Composite, 1 in. ²	35
↓	32
	29
	52
Stainless Steel, 2 in. ²	65
Stainless Steel, Welded, 2 in. ²	82
Stainless Steel, Welded, 2 in. ²	92

TABLE II
FLUORIDE CONCENTRATION BY MICROPROBE ANALYSIS

<u>Specimen Material</u>	<u>Relative Fluoride Intensity*</u>
Stainless Steel End of Composite	1.00**
Stainless Steel, Welded, away from Weld	1.37**
Stainless Steel, Welded, near Weld	9.91**
Copper End of Composite	2.80**
Copper, Brazed, away from Weld	5.41
Copper, Brazed, near Weld	5.57**
Copper	5.02**
Aluminum	23.23**

*Measured intensities were adjusted to give a unit value to the minimum reading (stainless steel portion of a composite specimen). No absolute measurements were taken.

**Average of two measurements.

Metallographic examination of specimen cross sections showed no indications of pitting, intergranular corrosion, or stress-corrosion cracking. Photomicrographs at 500X magnification are shown in Figs. 8 through 12. Figure 8 shows a control specimen and may be compared with Fig. 9, which shows a similar specimen from the test. There were no indications of significant corrosion from pitting or intergranular attack either at the welds or away from the welds. Figure 10 shows the cross section of a weld in an unexposed control specimen. Figures 11 and 12 show similar photomicrographs taken of a test specimen at the weld and away from the weld. No effect was noted as a result of imposing external stress on the specimens, as is evidenced by Figs. 10, 11, and 12.

The slight degree of surface grain boundary notching and surface irregularity appearing in the photomicrographs is characteristic of the raw shim stock and showed no tendency to change during the test.

Although no corrosion of structural importance was detected, the light surface film would cause some loss in surface optical properties such as reflectivity and absorptivity. These are often important in the overall performance of a cryopanel.

6.2 COPPER SPECIMENS

All copper specimens were mildly tarnished, as shown in Figs. 13 and 14. This would affect the optical properties of the copper surfaces. There was no evidence of scale formation, indicating that the film was thin and adherent. Those areas protected by the holder fin were relatively untarnished and retained their metallic luster.

The copper shim stock showed no indications of structural corrosion. Figures 15 and 16 show an unexposed control and an unstressed test specimen at 500X magnification. There are no grain boundary corrosion effects and no pitting. The slight surface roughening is typical of specimens cleaned in acetic acid solution before testing.

Figure 17 is a photomicrograph of a phosphor bronze welded copper specimen taken near the weld. Here again, there is no indication of corrosive action. This specimen is the same one that appears in Figs. 18 and 19 and was under bending stress during the F₂ exposure. The presence of stress apparently exerted no influence on corrosion activity in any of the copper specimens tested. The grain enlargement appearing in the specimen in Fig. 17 resulted from the welding heat and is characteristic of metals in the vicinity of weldments.

The welds showed a moderate degree of component segregation or coring. This occurs during nonequilibrium cooling of multicomponent welds, and, in this instance, consists of a slight segregation of the tin in the weld. Coring is more pronounced near the toe of the weld (Fig. 18) where a dendritic structure is apparent. Here the tin-rich areas appear as dark zones. The center of the weld (Fig. 19) showed less segregation. A previous study with nitrogen tetroxide corrodent (Ref. 13) had revealed some pitting corrosion at the tin-rich sites. This was not found with F_2 , although careful microscopic examination was done at magnifications up to 1000X.

Total fluoride analyses on the copper test specimens showed higher values for the brazed specimens, as presented in Table I. Since the pretest cleaning removed all of the gross oxide formed during brazing, the higher fluoride levels are not associated with residual welding oxide as was the case with the welded stainless steel specimens. It is believed that the higher fluoride concentration in the brazed samples is related to the tin segregation in the phosphor bronze weldment. The electron microprobe analysis showed a higher relative fluoride intensity near the weld than on the base metal remote from the weld (Table II). Higher fluoride concentration would be expected because of the higher valence state of tin as compared to copper and also to the greater surface area (roughness) of the weld bead. In any event, the higher fluoride concentration near the weld did not result in detrimental structural corrosion.

6.3 COPPER/STAINLESS STEEL COMPOSITE SPECIMENS

Metallographic examination of each component of the composite specimens revealed no difference in the corrosive action compared to single specimens of the same material. No pitting, stress-corrosion cracking, or intergranular corrosion was found in either the stainless steel, the copper, or the nickel weldment. The copper portions were tarnished in the same manner as the all-copper specimens, Fig. 20. The stainless steel portion was covered with a light film. Figures 21 and 22 show photomicrographs of unexposed control specimens at the welds. These may be compared with Figs. 23 and 24 showing similar regions of test specimens which were exposed to F_2 under applied stress. Figures 25 and 26 show that the base metals were unaffected by exposure and stress. These may be compared with control specimens shown in Figs. 15 (copper) and 8 (stainless steel).

No differences were noted as a result of stressing, and no differences were found between those specimens contacting copper holder fins and those contacting stainless steel fins during exposure.

As would be expected, the relative fluoride intensity found on the copper surface was higher than on the stainless steel surface. The higher total fluoride found on the stainless steel-plus-weldment sample than on the copper tip is, thus, probably caused by F_2 attack on the weld. The weldment and the adjacent stainless steel base metal would take up more F_2 because of the presence of welding oxide, caused by a higher surface area at the weld, and, perhaps, caused by the reactivity of the nickel weld with F_2 . However, the analytical data do not permit a distinction to be made between these mechanisms.

6.4 SERIES 1100 ALUMINUM SPECIMENS

The aluminum specimens all had a light, hazy surface film as a result of exposure, as shown in Fig. 27. Fluoride analyses of this film yielded the highest levels of fluoride found on any specimen. The presence of this film led to a suspicion that HF had been formed in the test chamber at some time during the test, probably as a result of in-leakage of atmospheric moisture. A verification of the presence of HF was made by exposing several clean aluminum specimens to 0.5 atm of dry F_2 at about 70°C for 48 hr. The specimens were bright and visibly unaffected after this exposure. However, the white film was formed very rapidly on the surface of specimens dipped in hydrofluoric acid at room temperature.

Despite the attack apparent from the surface film, metallographic examination revealed no evidence of structural corrosion other than a slight roughening of the surface. Control and test specimen photomicrographs are shown in Figs. 28 and 29.

The formation of the fluoride surface film may be expected in actual propulsion tests where unprotected aluminum cryopanel surfaces are used, since water will be present from the reaction products and from chamber in-leakage. While this may cause no structural difficulties, it will cause considerable change in the optical properties of the cryopanel surfaces.

6.5 STAINLESS STEEL CRYOPANEL SPECIMEN

There was no evidence of significant corrosive attack on the stainless steel cryopanel material. A light haze, similar to that found on the stainless steel shim, was present. Photomicrographs of a control specimen and the test specimen are shown in Figs. 30 and 31. Metallographic examination of sections at the welds indicated no corrosive action on weldments. No fluoride determinations were made on the surface film.

SECTION VII

SUMMARY AND CONCLUSIONS

While it should be noted that these results will not necessarily apply to conditions substantially different from those under which this test was conducted, the following conclusions may be drawn:

1. Stainless steel type 304L showed good resistance to F_2 corrosion. Applied stress did not enhance reactivity, and no evidence of stress-corrosion cracking was found. Welds made with 308 ELC wire maintained their integrity throughout the test. A thin, translucent film was formed which probably would affect the optical characteristics of the surface.
2. Phosphorus deoxidized copper was tarnished noticeably, but no pitting, intergranular corrosion, or stress-corrosion cracking occurred. There was more reactivity at the braze welds, as evidenced by fluoride analyses, but the extent of attack was not serious. Some change in the surface properties may be expected from tarnishing.
3. Copper/stainless steel 304L composites joined with nickel wire showed generally the same results in their component parts as the individual materials tested separately. The nickel weld showed no structural corrosion. No effect was induced by stressing or by contact with different fin materials.
4. Series 1100 aluminum was coated with a white fluoride film which caused a loss of the metallic surface luster. There is strong evidence that this resulted from contact with HF formed during the test. The metal did not exhibit any localized corrosive attack other than a slight surface roughening.
5. A type 304L stainless steel cryopanel was virtually unaffected by exposure except for the formation of a thin, adherent, and translucent surface film.
6. Based on this test, type 304L stainless steel appears to be less affected than aluminum 1100 and phosphorus deoxidized copper. The 304L stainless steel should have a longer service life as a cryopanel material and should suffer less change in surface optical properties.

REFERENCES

1. Gundzik, R. M. and Feiler, C. E. "Corrosion of Metals of Construction by Alternate Exposure to Liquid and Gaseous Fluorine." NACA TN 3333, December 1954.
2. Jackson, R. B. "Corrosion of Metals and Alloys by Fluorine." Allied Chemical Corporation, General Chemical Division, Hopewell, Virginia, March 1960.
3. Landau, R. "Corrosion by Fluorine and Fluorine Compounds." Corrosion, Vol. 8, No. 8, August 1952, pp. 283-288.
4. Mason, R. W. and Staiti, J. J. "Study of the Corrosion of Metals in Fluorine." Allied Chemical Corporation, General Chemical Division, Morristown, New Jersey, February 7, 1959.
5. Myers, W. R. and DeLong, W. B. "Fluorine Corrosion." Chemical Engineering Progress, Vol. 44, No. 5, 1948, pp. 359-362.
6. Price, H. G., Jr. and Douglass, H. W. "Material Compatibility with Gaseous Fluorine." NACA-RM-E56K21, January 1957.
7. Sterner, C. J. and Singleton, A. H. "The Compatibility of Various Metals and Carbon with Liquid Fluorine." WADD TR 60-436, August 1960.
8. Whitaker, G. C. "Corrosion of Metals in Fluorine and Hydrofluoric Acid." Corrosion, Vol. 6, No. 9, September 1950, pp. 283-285.
9. "Compatibility of Materials with Rocket Propellants and Oxidizers." Defense Metals Information Center, Battelle Memorial Institute, Columbus, Ohio, DMIC Memorandum 201, January 1965.
10. Schmidt, H. W. and Harper, J. T. "Handling and Use of Fluorine and Fluorine-Oxygen Mixtures in Rocket Systems." NASA SP-3037, 1967.
11. Cabaniss, J. H. and Williamson, J. G. "A Literature Survey of the Corrosion of Metal Alloys in Liquid and Gaseous Fluorine." NASA TM X-54612, December 1963.
12. Andreeva, V. V. "Behavior and Nature of Thin Oxide Films on Some Metals in Gaseous Media and in Electrolyte Solutions." Corrosion, Vol. 20, No. 2, 1964, pp. 35t - 46t.
13. Waldrep, P. G. and Trayer, D. M. "Nitrogen Tetroxide Corrosion Studies of Cryopanel Materials for Space Chamber Propulsion Testing." AEDC-TR-68-138 (to be published).

**APPENDIX
ILLUSTRATIONS**

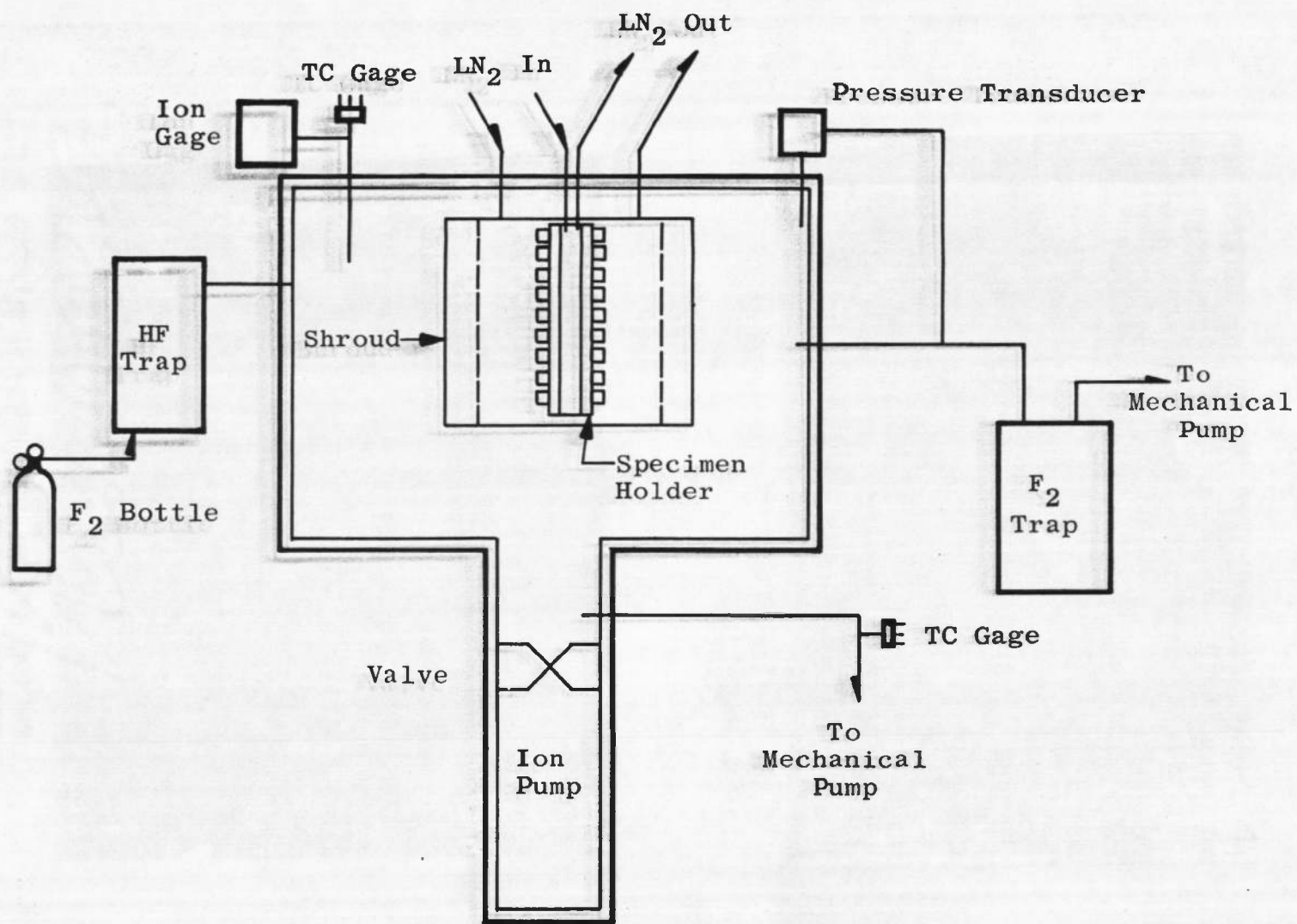


Fig. 1 Fluorine Corrosion Test Chamber Schematic

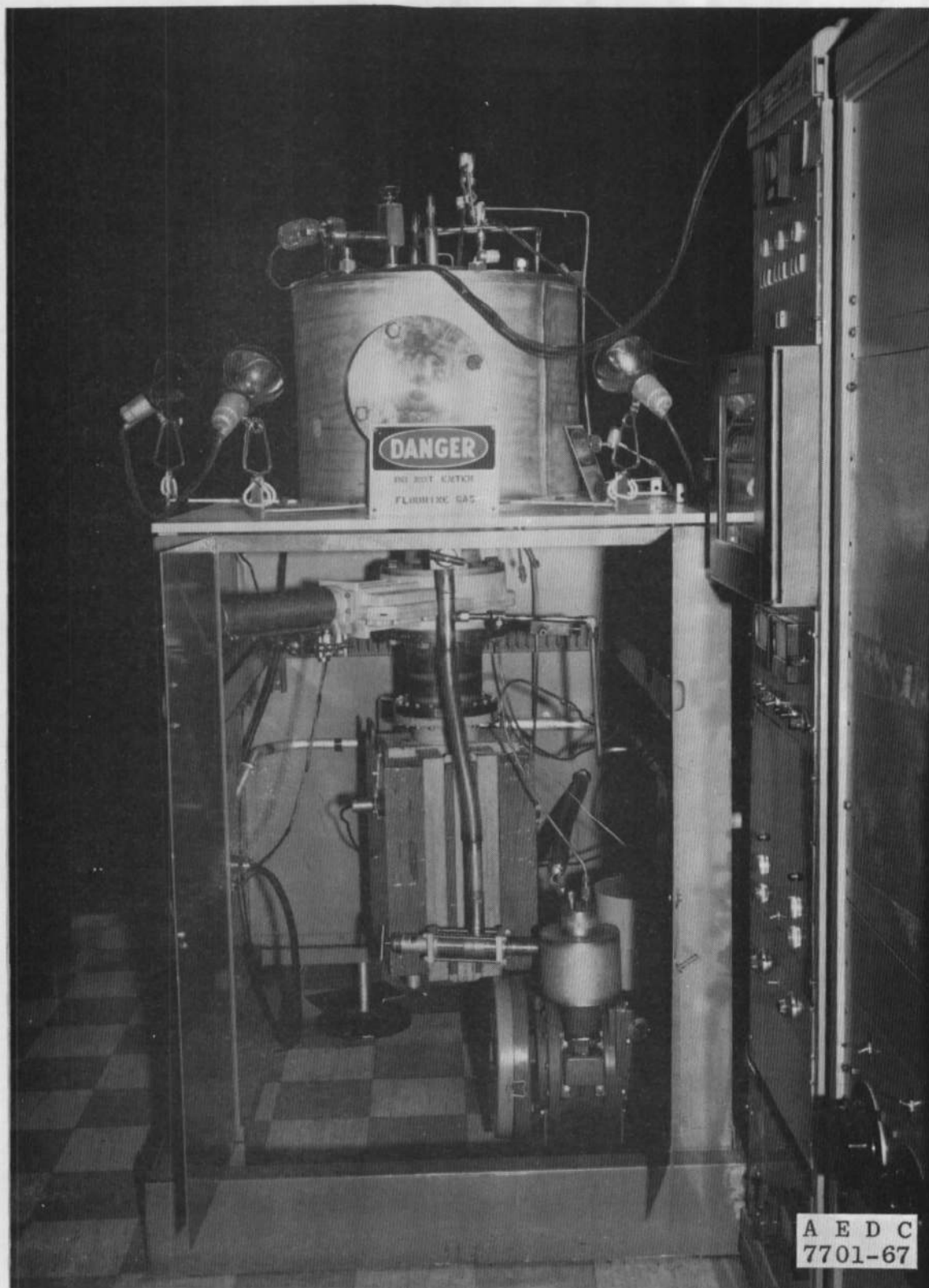


Fig. 2 2- by 1.5-Foot Research Vacuum Chamber

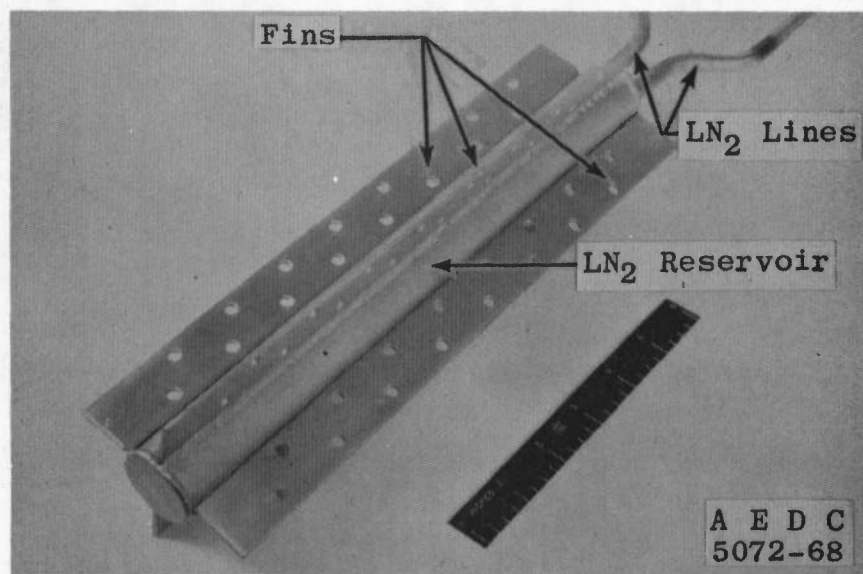


Fig. 3 Specimen Holder

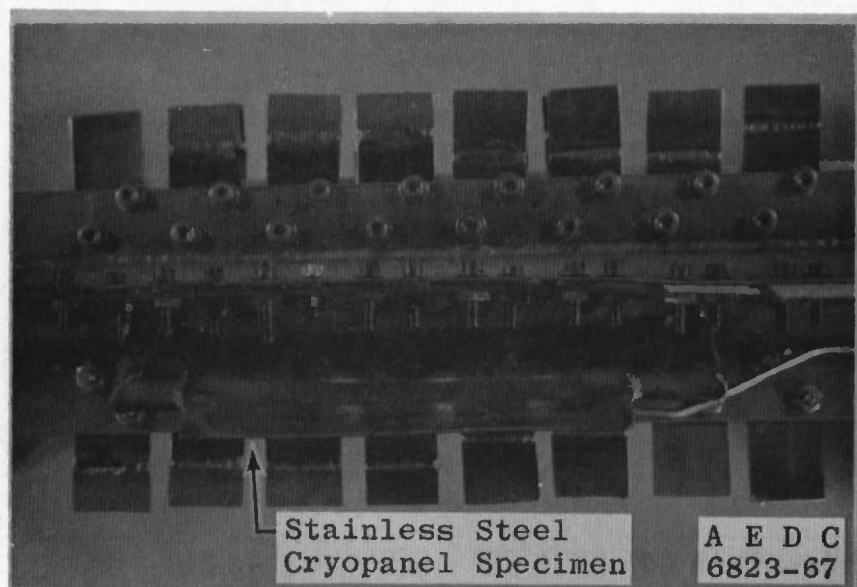


Fig. 4 Specimens Mounted on Holder

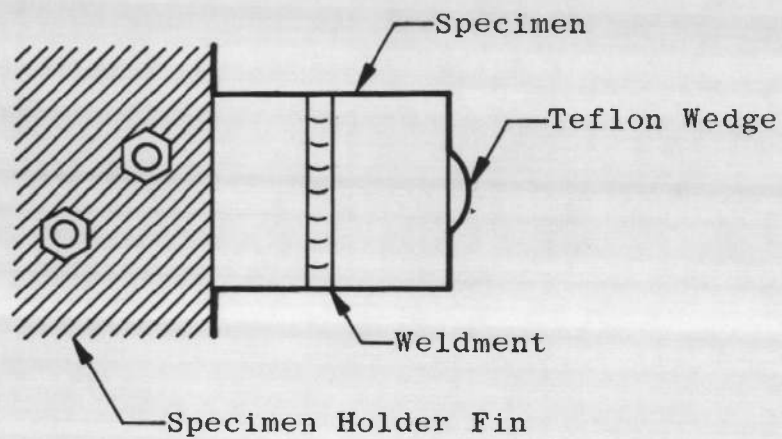
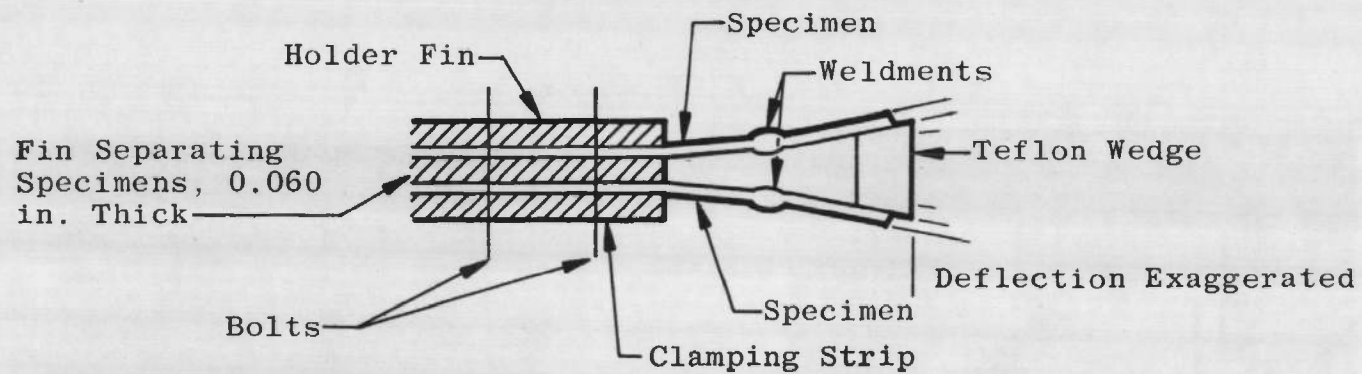


Fig. 5 Schematic Views of Specimens Stressed for F_2 Corrosion Testing



Fig. 6 Unwelded Stainless Steel 304L, Exposed to F_2 , 2X

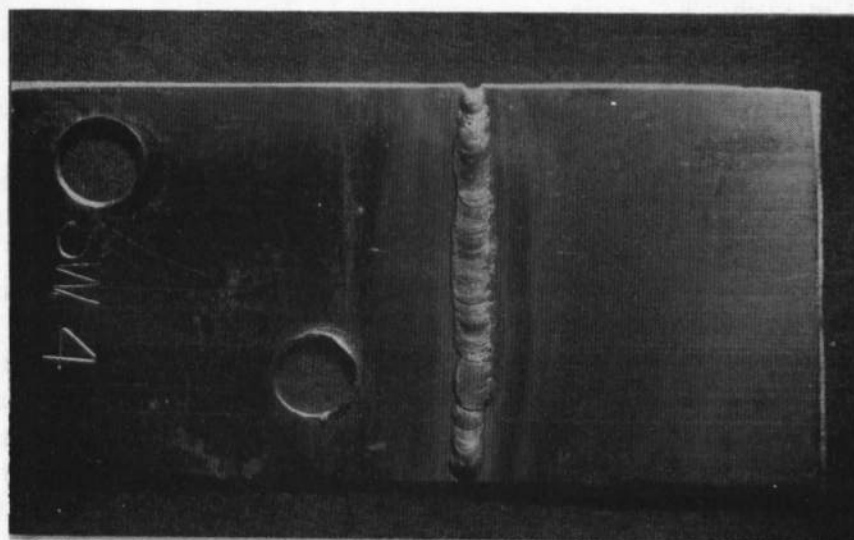


Fig. 7 Welded Stainless Steel 304L Specimen, Exposed to F_2 , 2X

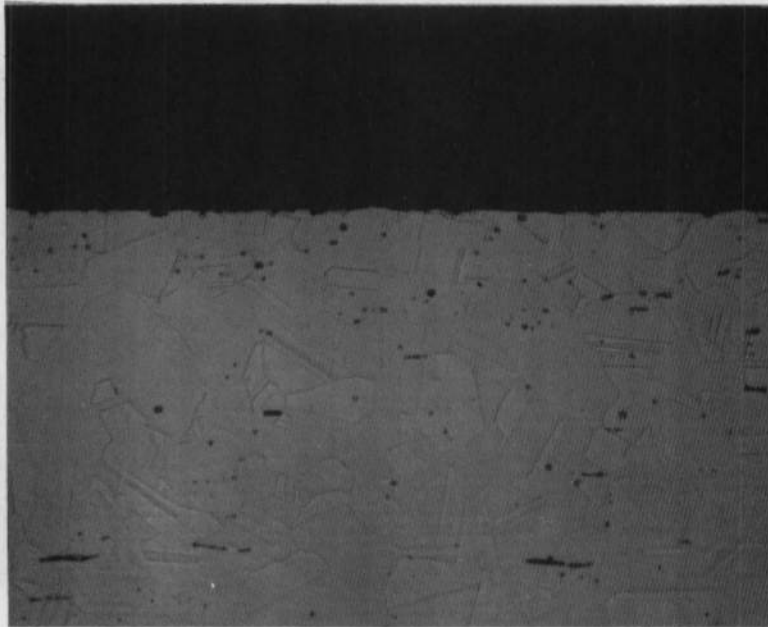


Fig. 8 Control, Unwelded Stainless Steel 304L, Unexposed, 500X

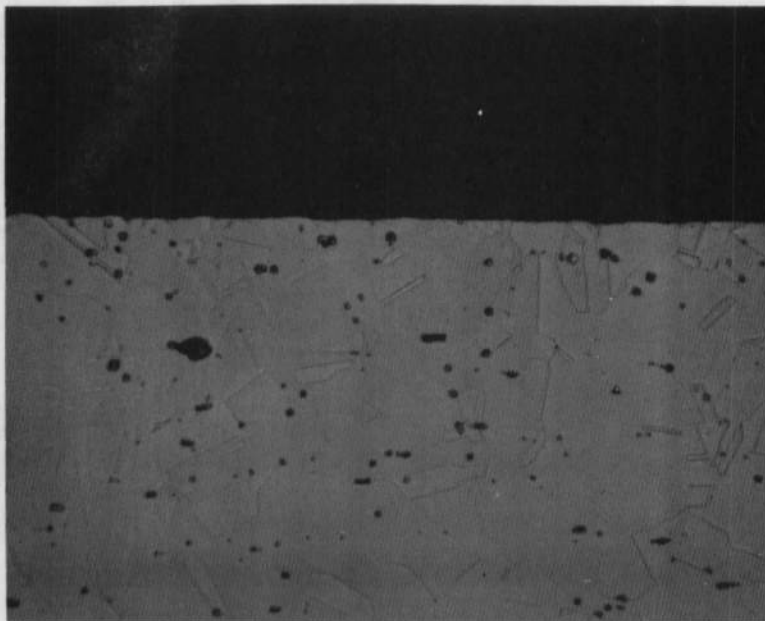


Fig. 9 Unwelded Stainless Steel 304L, Exposed to F_2 , 500X

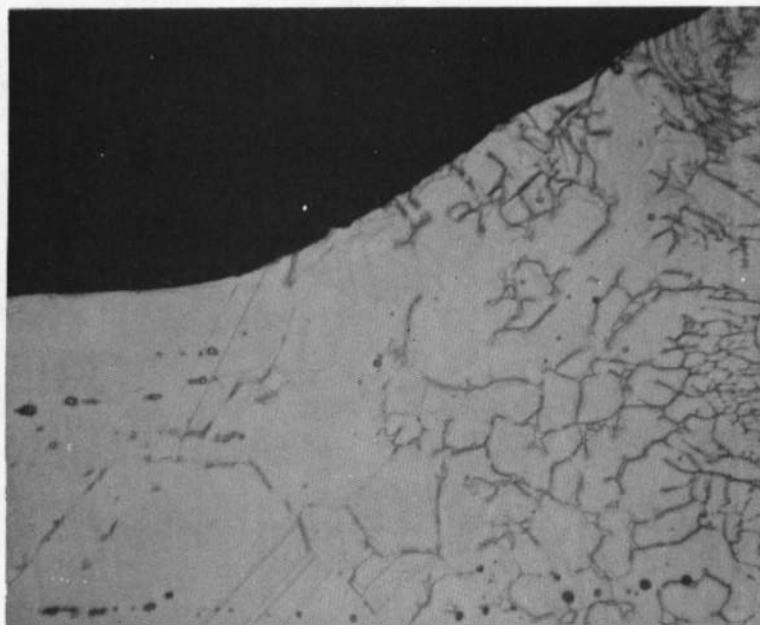


Fig. 10 Control, Welded Stainless Steel 304L,
at Weld, Unexposed, 500 X

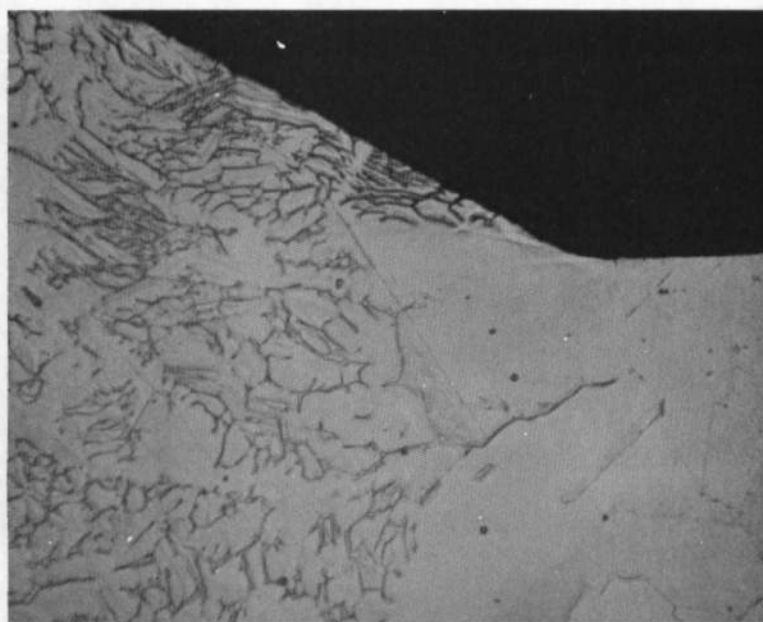


Fig. 11 Welded Stainless Steel 304L, Stressed,
at Weld, Exposed to F₂, 500 X

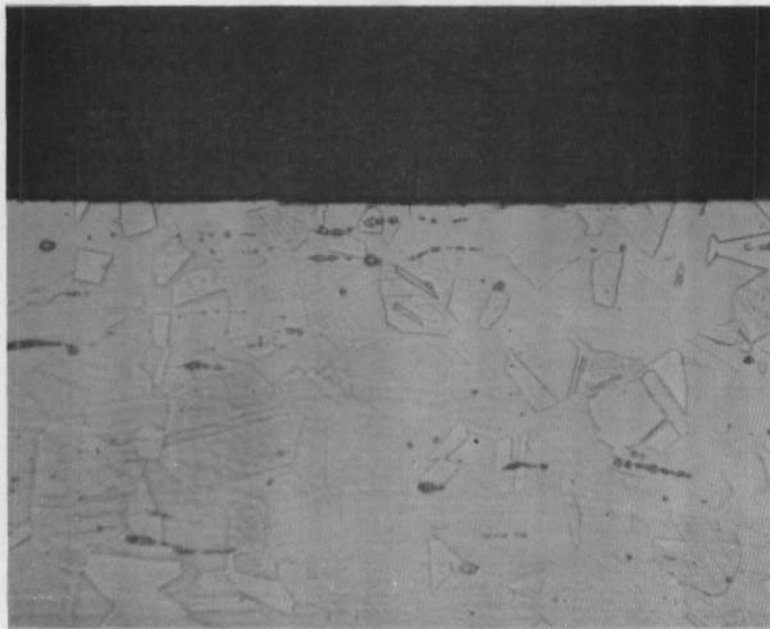


Fig. 12 Welded Stainless Steel 304L, Stressed,
Away from Weld, Exposed to F_2 , 500X

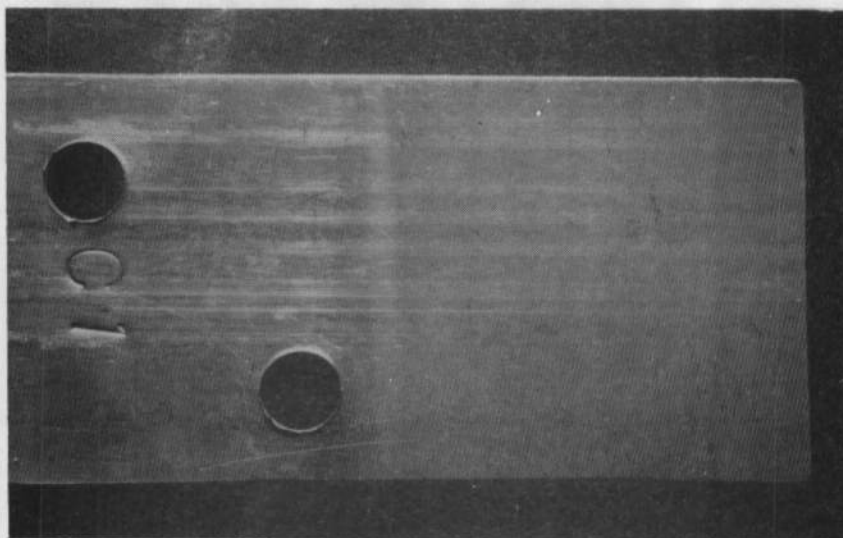


Fig. 13 Unwelded Copper Specimen, Exposed to F_2 , 2X

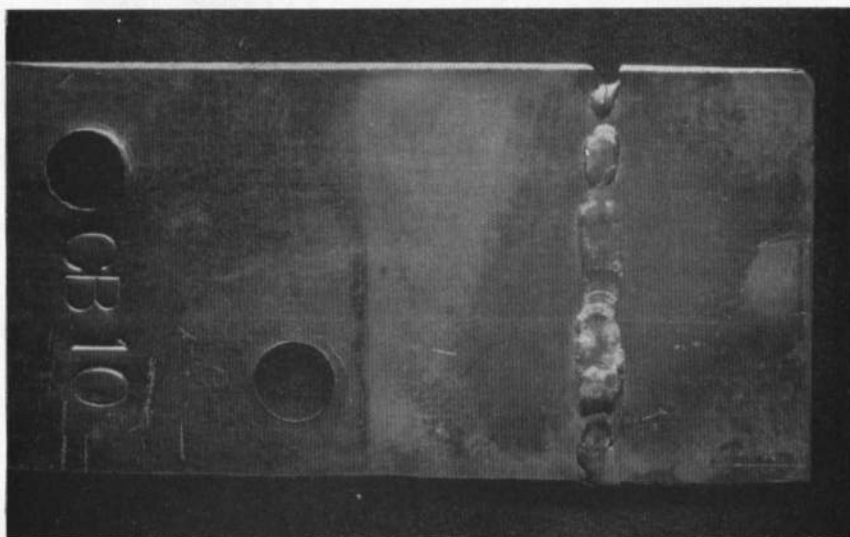


Fig. 14 Brazed Copper Specimen, Exposed to F_2 , 2X

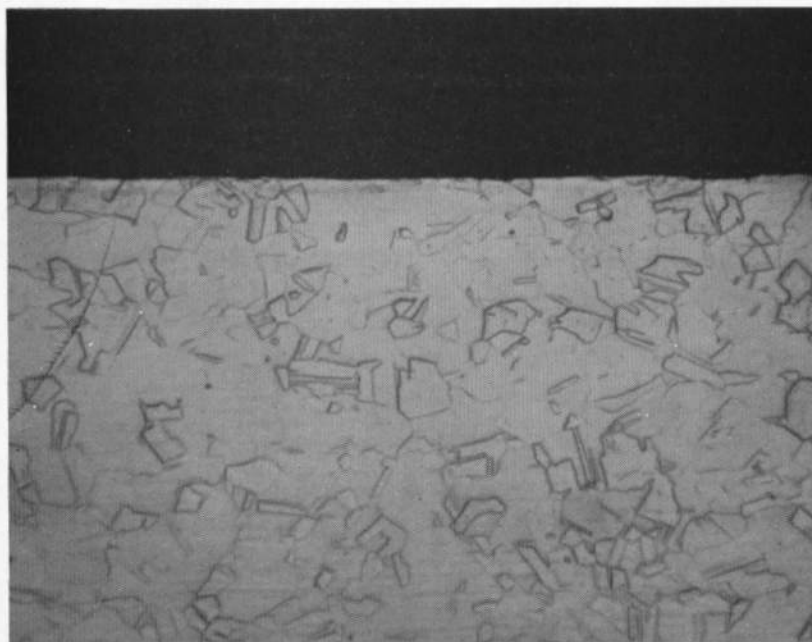


Fig. 15 Control Copper Specimen, Away from
Braze Joint, Unexposed, 500X

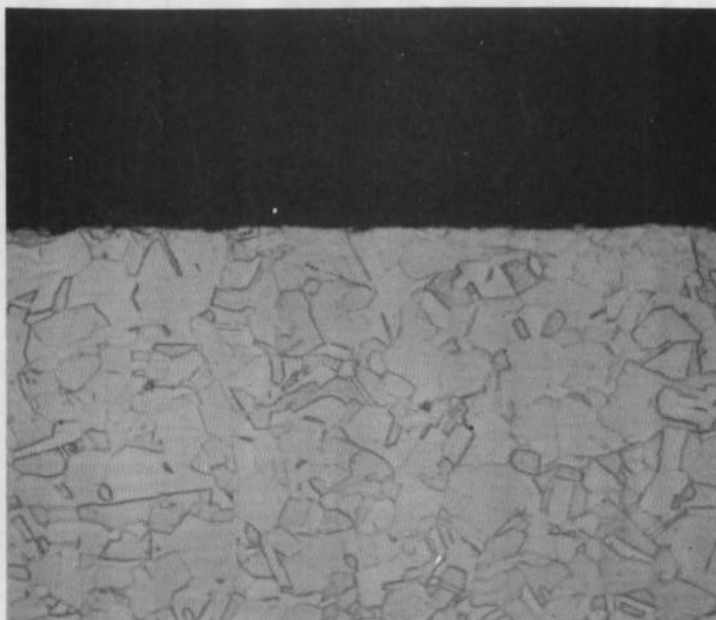


Fig. 16 Unwelded Copper Exposed to F₂, 500X

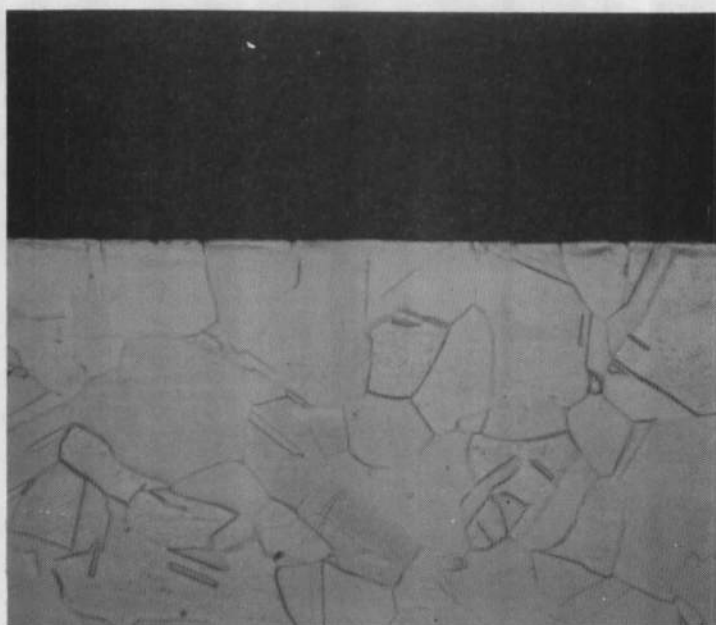


Fig. 17 Bronze Welded Copper, Near Weld, Stressed,
Exposed to F₂, 500X

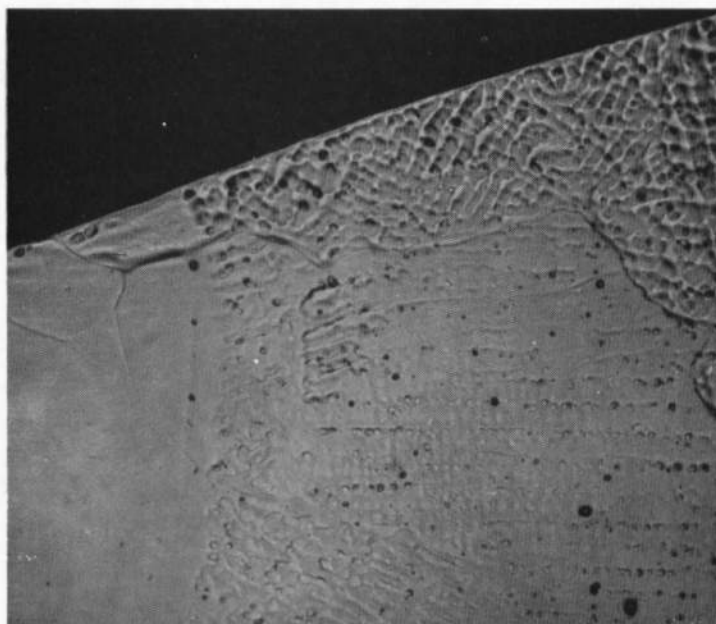


Fig. 18 Toe of Phosphor Bronze Weld, Stressed,
Exposed to F_2 , 500X

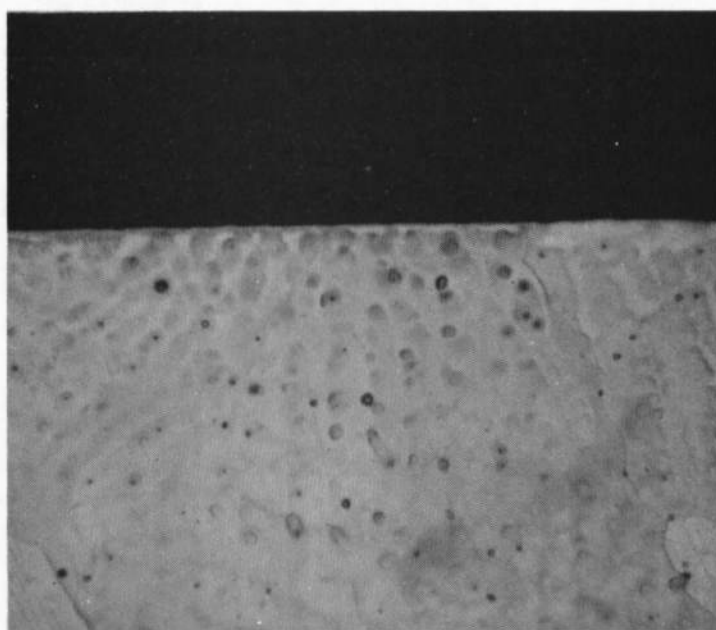


Fig. 19 Center of Phosphor Bronze Weld,
Stressed, Exposed to F_2 , 500X

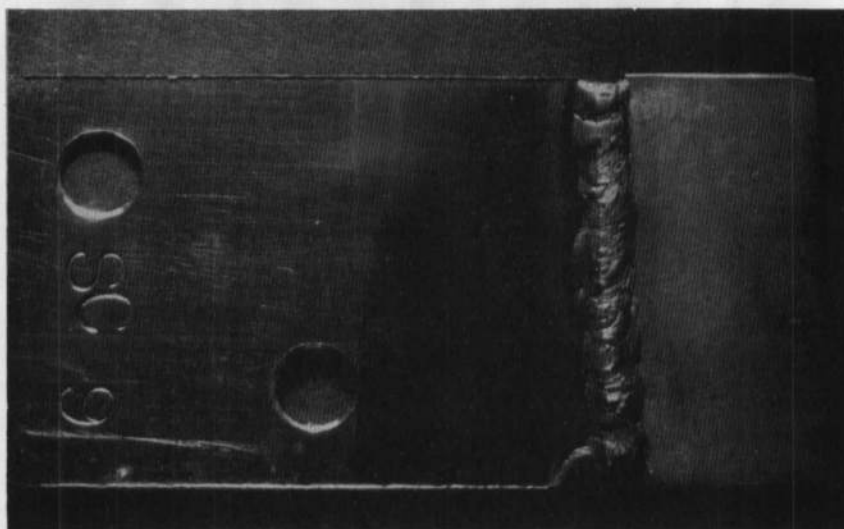


Fig. 20 Copper-Stainless Composite Specimen,
Exposed to F_2 , 2X

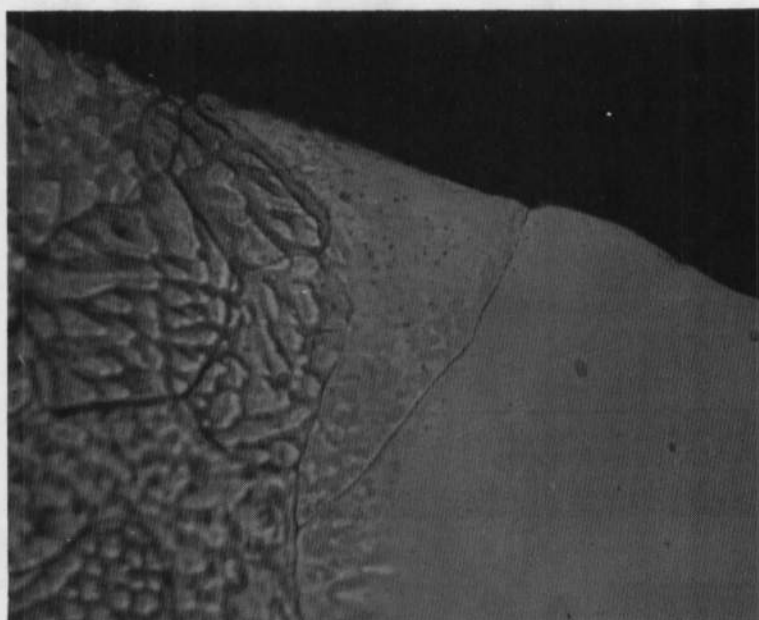


Fig. 21 Control Specimen, Copper Side of Nickel
Weldment, Unexposed to F_2 , 500X

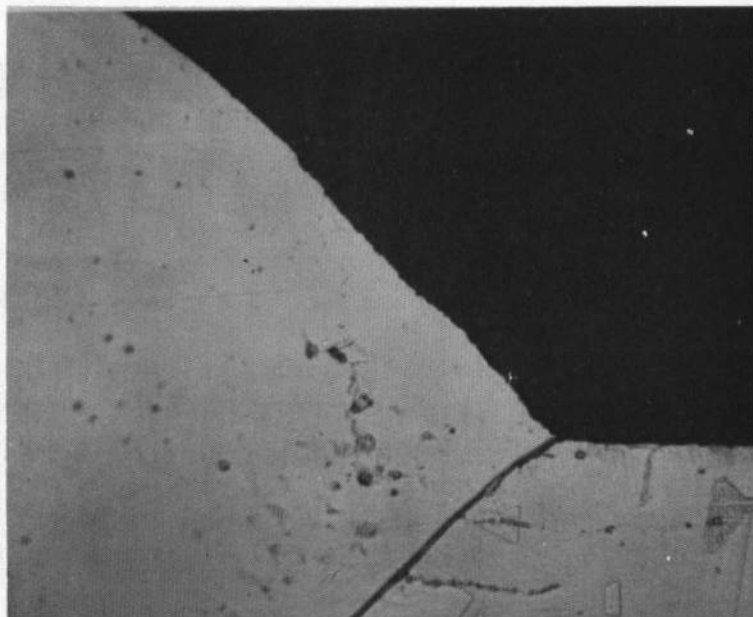


Fig. 22 Control Specimen, Stainless Steel Side of Nickel Weldment, Unexposed to F_2 , 500X

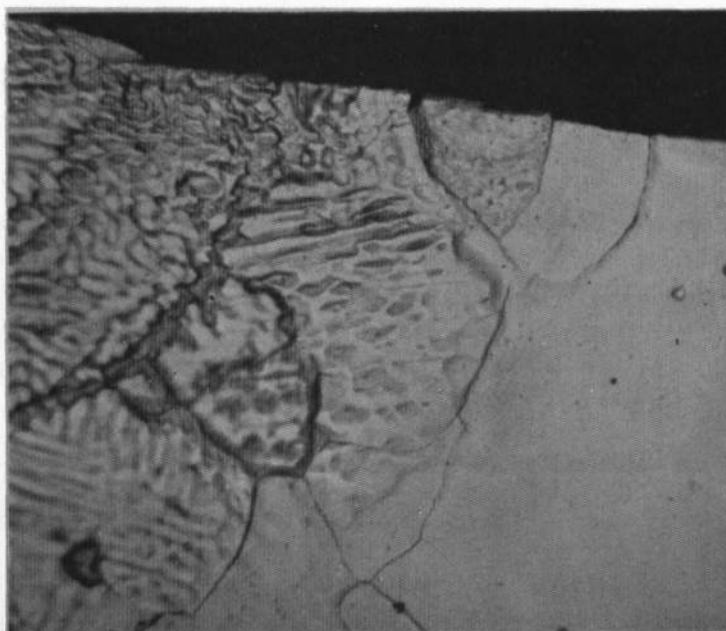


Fig. 23 Copper Side of Nickel Weldment, Exposed to F_2 , Stressed, 500X

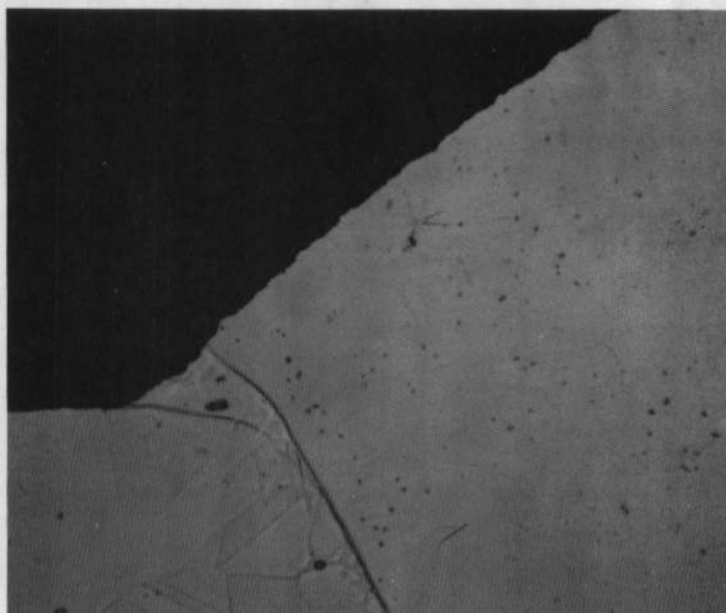


Fig. 24 Stainless Side of Nickel Weld,
Exposed to F_2 , Stressed, 500X



Fig. 25 Copper Shim Portion of Composite Specimen, Away
from Weld, Exposed to F_2 , Stressed, 500X

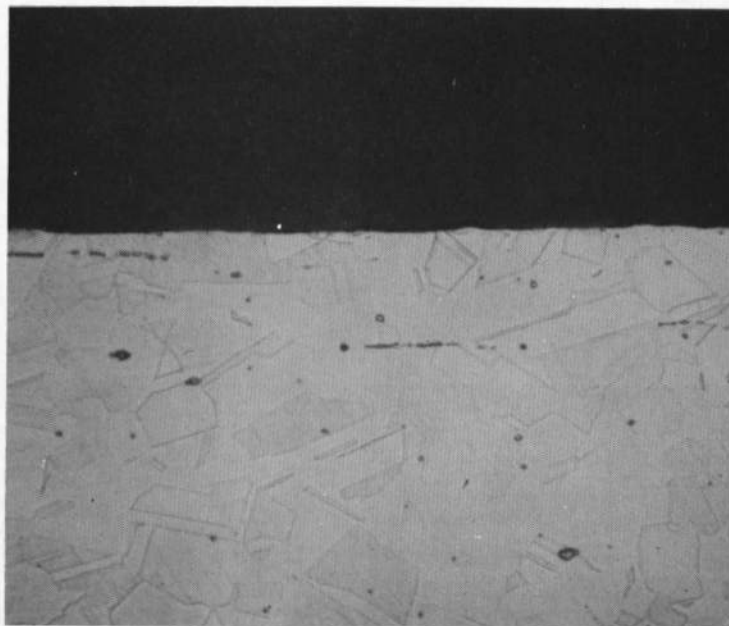


Fig. 26 Stainless Shim Portion of Composite Specimen, Away from Weld, Exposed to F_2 , Stressed, 500X

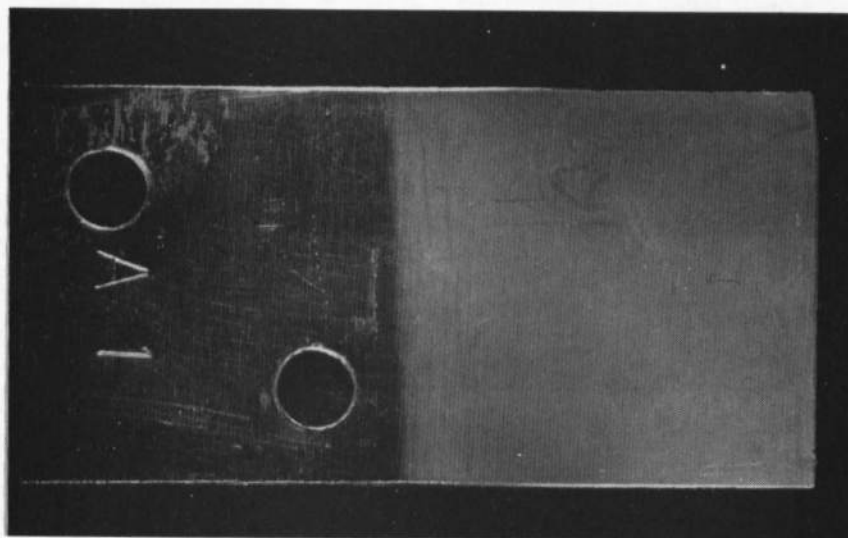


Fig. 27 Aluminum Specimen, Exposed to F_2 , 2X

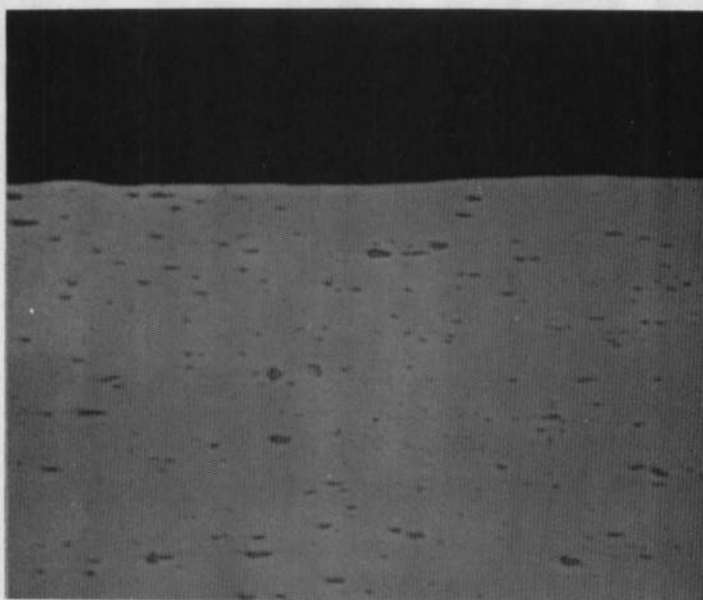


Fig. 28 Control Specimen, Unexposed
Aluminum, 500X

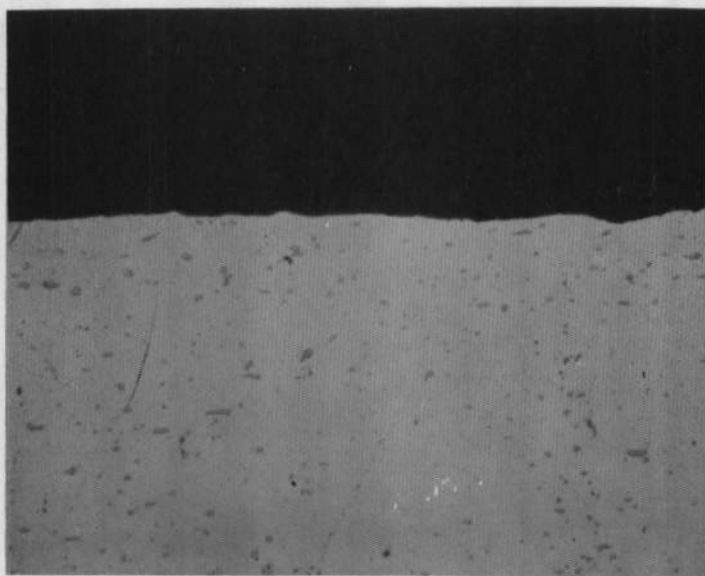


Fig. 29 Aluminum Exposed to F_2 , 500X

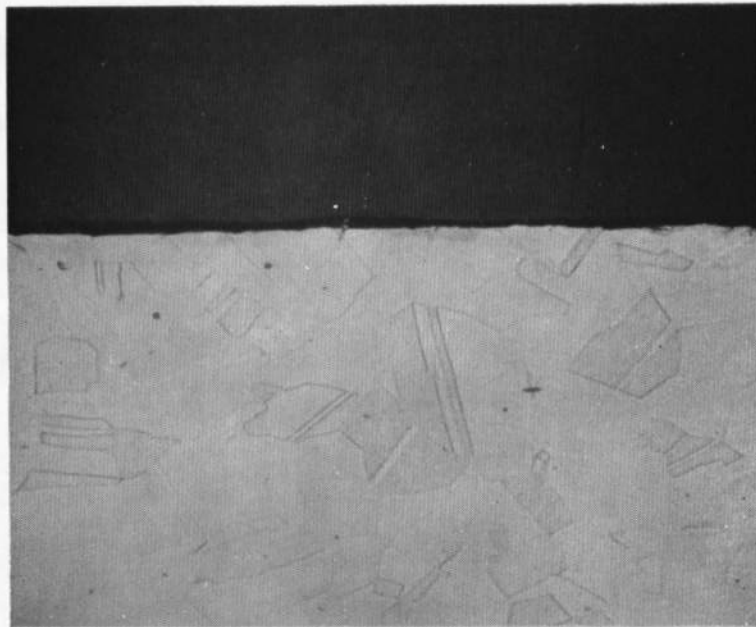


Fig. 30 Control, Stainless Steel Cryopanel,
Unexposed, 500X

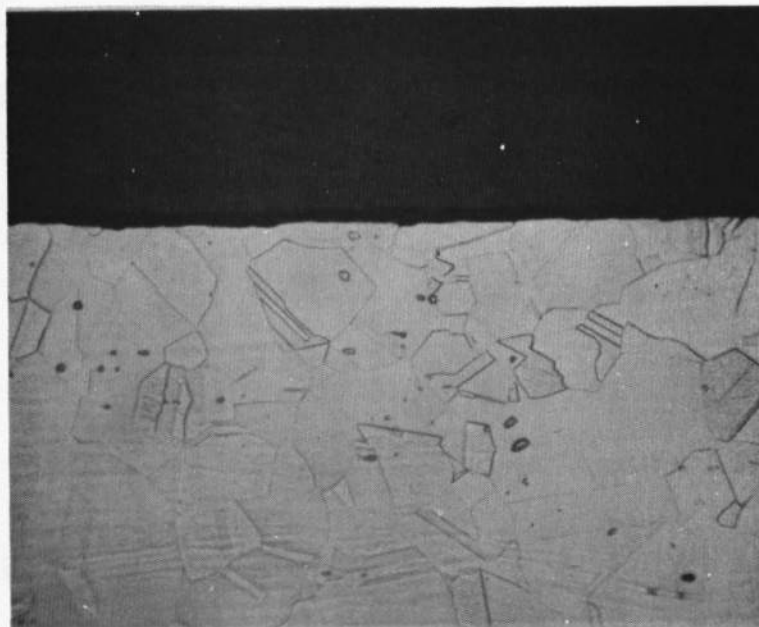


Fig. 31 Stainless Steel Cryopanel,
Exposed to F_2 , 500X

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Arnold Engineering Development Center, ARO, Inc., Operating Contractor, Arnold Air Force Station, Tennessee		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP N/A	
3. REPORT TITLE INVESTIGATION OF THE EFFECTS OF FLUORINE ON CRYOPANEL MATERIALS FOR SPACE CHAMBER PROPULSION TESTS			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) January to August 1967 - Final Report			
5. AUTHOR(S) (First name, middle initial, last name) P. G. Waldrep and D. M. Trayer, ARO, Inc.			
6. REPORT DATE September 1968		7a. TOTAL NO. OF PAGES 42	7b. NO. OF REFS 13
8a. CONTRACT OR GRANT NO. F40600-69-C-0001		9a. ORIGINATOR'S REPORT NUMBER(S) AEDC-TR-68-174	
b. PROJECT NO. 5730			
c. Program Element 62302F		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) N/A	
d. Task 573004			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its dis- tribution is unlimited.			
11. SUPPLEMENTARY NOTES Available in DDC.		12. SPONSORING MILITARY ACTIVITY AEDC (AETS), Air Force Systems Command, Arnold AF Station, Tennessee 37389	
13. ABSTRACT The extent of corrosion by fluorine (F ₂) on several cryopanel materials was evaluated for conditions approximating those which might be expected in a space simulation chamber during rocket engine tests. Four torr of F ₂ pressure was applied at room temperature; and specimen temperatures were cycled between ambient and 77°K. The chamber was periodically pumped to high vacuums. The total exposure time exceeded 1000 hr. Type 304L stainless steel, phosphorus deoxidized copper, and 1100 aluminum were tested. Some specimens were welded, and some were tested with an applied bending stress. No pitting or other microstructural corrosion was detected, but noticeable changes occurred in the surface appearance, especially with aluminum and copper.			

14.

KEY WORDS

space chambers
propulsion tests
cryopanel materials
fluorine effects

LINK A

LINK B

LINK C

ROLE

WT

ROLE

WT

ROLE

WT